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Value extraction from waste in the steelmaking industry

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Abstract: As the standard of living improves worldwide, the current emphasis on sustainable growth is creating new opportunities in traditional industrial practices. In steelmaking, where the production of solid waste is inevitable, extracting more value from metallurgical by-products appears vital to cope with the advances in the field of environmental regulation in the 21st century. Waste slag containing up to 30 wt. % titanium dioxide is available in its molten state, as the main by-product of New Zealand Steel's steelmaking process. Based on the current titanium (Ti) price, extracting high purity metal from slag is a promising alternative to the incumbent Kroll process and has the potential of exponentially increasing the by-product's value. In this study, we explore the electrolytic separation of Ti in light of the vast availability of the Ti-rich mixture contained within the waste slag. Specifically, we present the features and challenges of electrolyzing complex, not sufficiently studied, slag mixtures at ultra-high temperature.

Keywords: titanium extraction, molten oxide electrolysis, titanomagnetite sands, ultra-high-temperature processing.

1 Introduction

Optimizing the use of natural resources by recycling industrial waste seems essential to meet the current demand of materials in a sustainable manner. Promoting the use of waste slag from the ironmaking process as feedstock for further metal extraction aligns well with the values of the circular economy. During the 20th century alone, the world's population grew from 1.65 billion to 6 billion [1] and consequently the need for structural materials has increased exponentially. To meet that demand, several metallurgical processes have been developed and implemented to extract metals from their natural deposits. However, metallurgy is an energy, carbon, and waste-intensive sector and, today, the annual demand on resources exceed what Earth can regenerate in a year [2]. In an effort to meet the requirements for sustainable growth, pathways toward deep decarbonisation, waste minimization and reutilization are enforced by environmental regulation and encouraged by international agreements [3].

Steel is the most widely used alloy in the world, with a yearly production of 1700 million tonnes in 2017 [4]. Accordingly, in the order of 300 to 360 million tons of ironmaking slag and 170 to 250 million tons of steelmaking slag are estimated to be the by-product's output [4]. Solid waste management in the steelmaking industry must be considered in order to meet the current needs without compromising the ability of future generations to meet their own needs. New Zealand has the capacity to produce 650000 tonnes/year of iron and steel products [5]. This process is unique in that it uses titanomagnetite (ironsand) natural deposits as the main source of iron and so, up to 30 wt. % titanium dioxide (TiO_2) is available in its molten state as a component of the ironmaking slag. The TiO_2 content in the slag is too low to economically justify further processing to extract titanium dioxide with the current technology. Obtaining the high-value titanium metal [4], however, would be ground-breaking considering the high extraction and high processing costs of the current commercial process [6].

This work introduces the direct extraction of titanium from slag by ultra-high-temperature electrolysis. A process with the potential of minimizing environmental industrial impact by further utilization of titanomagnetite natural resources. Extracting not only iron but titanium would inevitable increase the value of ironmaking process's most abundant by-product. The major innovation of this project is the direct use of the waste fused slag, available at approximatively 1750 K, as feedstock. Due to the mixed oxide nature of the slag, it is hypothesized that no additional electrolyte is needed. That increases the sustainability of the process, upgrades an industrial by-product and eliminates the conventional first step of the extraction processes making the process simpler and more efficient.

2 Slag as a resource

For every ton of iron produced in the smelter approximatively 300 kg of ironmaking slag is formed [7]. Without proper recycling, this large amount of slag can become a significant source of waste. Increasing global environmental awareness is forcing the metallurgical industry to meet their environmental responsibility. This may be achieved, in part, by minimizing and reutilizing the slags. Piatak et al. [8] extensively characterized the different types of industrial slags and their environmental consequences. Nevertheless, it is still today a great challenge to both recover the heat from the molten slag and utilize the solidified slag [9].

Ironmaking slag accounts for 10% of the waste energy in the steel industry since it is drained in its molten state at temperatures above 1500 K [10]. The opportunities for managing this waste have been studied before [11,12,13]; however, the existing heat recovery technologies are still at their infancy [9,10]. Uncontrolled heat treatments such as dumping and water quenching are the conventional methods for disposal of slag. In Europe where the reutilization ratio is high, still 35% of these slags are dumped [14]. The lack of land available for disposal, the shortage of water and the environmental concerns are preventing the continuity of these mainstream methods [15]. Alternatively, interest has increased towards studying dry granulation as a substitutional technology [16]. Despite that, its maturity is limited to cost-effective uncertainties [4].

The solidification step defines the applications for ironmaking slag. Uncontrolled heat treatments have limited slag recycling to civil engineering applications, such as road construction, since Roman times [11]. Fast cooling rates facilitates the vitreous solidification of the silica glass. Due to the similar chemical composition of the slag to that of cement, fast-cooled slag meets the hydraulic properties required for cementing components [17]. Controlled heat treatments find another field of application by controlling the crystallization process [7]. Manufacturing glass-ceramics materials from slag has expanded since its invention in 1960s. Still, the detrimental effect of the presence of iron and the required low basicity (CaO/SiO_2 wt. % below 0.5) needed limits the rate of utilization of the slag [9].

Furthermore, to process the solidified slag remains a challenge. The recycling of slag in the steelmaking process as a source of calcium or manganese can reduce the material cost but it can be harmful for the mechanical properties of the steel since phosphorus and sulphur are normally contained within the slag [18]. Additionally, poor volume stability caused by the expansion of CaO after hydration limits its reutilization [7]. From the literature, it seems obvious that a different approach is needed to find a solution to further utilization.

3 Slag as a source

From propeller shafts and power plant condensers to medical implants and aircrafts [19], it is astounding how reliant society is on the use of the 22nd element of the Periodic Table. Titanium is the fourth-most abundant metal in the earth's crust and the ninth-most common element on the entire planet, but it was not discovered until 1791, as part of a black sand called menachanite [20]. Titanium is, indeed, present in many igneous rocks and sediments, primarily found in the minerals sphene ($CaTiSiO_5$), ilmenite ($FeTiO_3$) and rutile (TiO_2). Mining of titanomagnetite mineral deposits, present along the west coast of the North Island, are New Zealand's main source of titanium and iron [21]. Before entering the ironmaking process, these ironsands are concentrated by gravity and magnetic separation. The chemical composition of the product, primary concentrate, was investigated using X-ray fluorescence (XRF) and is listed in Table 1 [22].

Table 1: Chemical composition of primary concentrate (wt. %).

TiO_2	Al_2O_3	CaO	SiO_2	MgO	FeO	MnO	V_2O_5
7.9	3.7	0.5	2.3	2.9	81.4	0.6	0.5

The Holy Grail of titanium production would be to use the mineral directly [23]. However, with the current industrial process, refining the ore into titanium metal is a costly, multistep, high temperature batch process that is energy and capital intensive [20]. According to a study by T.E. Norgate and G. Welwood [24], a 50% fall in the price of titanium can overcome its current restriction to high-added value applications, increasing its use by 200%. While such a price drop appears to be unrealistically large, their results show a great potential for market penetration influenced by the production cost. Thus, the need for new processes to produce cost-affordable titanium has attracted noteworthy research attention [25,26]. Table 2 provides an overview on the main routes studied.

Table 2: Research projects for titanium metal extraction.

Process Name/Organization	Description	
TIRO/CSIRO	Fluidized bed $TiCl_4$ reduction with Mg	[27]
Armstrong/ITP	$TiCl_4$ vapour reduction with Na	[28]
Idaho Titanium Tech	Hydrogen plasma reduction of $TiCl_4$	[29]
SRI International	Fluidized bed $TiCl_4$ reduction with H_2	[30]
Ginatta/GTT S.R.L.	$TiCl_4$ electrolysis in molten salt	[31]
Tresis International	Argon plasma reduction of $TiCl_4$	[32]
Polar Titanium/BHP Billiton	TiO_2 electrolysis in molten salt	[33]
CSIR	TiO_2 electrolysis in molten CaF_2	[34]
DMR	TiO_2 aluminothermic reduction	[32]
Preform Reduction/Tokyo University	TiO_2 reduction with Ca	[35]
EMR-MSE/Tokyo University	TiO_2 calciothermic reaction in molten salt	[36]
FFC/Metalysis	Sintered TiO_2 electrolysis in molten $CaCl_2$	[37]
MER Corp.	TiO_2 carbothermic reduction followed by electrolysis	[38]
OS/Kyoto University	TiO_2 calciothermic reduction in molten $CaCl_2$	[39]
Peruke (Pty) Ltd.	Fluotitanate reduction with Al	[40]
QIT/Rio Tinto	Molten Ti slag electrolysis	[41]
MOE/MIT	Direct electrolysis of molten Ti oxides	[42]
MIR-Chem	TiO_2 reduction with I_2	[43]
SCPS/Peking University	Selective crystallization and phase separation	[44]
HDH	Ti hydride–dihydride process	[45]

It is particularly hard to elucidate how advanced any project is since most of these developing processes have unpublished associated intellectual property (i.e. trade secrets). However, Table 2 illustrates that most of the precursors used in the new extraction projects do not occur naturally in the environment. Historically, it was thought that only by transforming the ore into a compound, which contains no oxygen or carbon, high purity grade metal could be yielded. Recent research has proven that wrong [37]. Furthermore, the use of different precursors could potentially halve the extraction cost since it is estimated that 52% of the sponge[1] production cost comes from the preparation of $TiCl_4$ [46]. Direct extraction from ore or slag would be the ideal solution because it would eliminate the costly production of intermediate precursors. Attempts have been made [41,42] but the maturity of the Kroll process and the development of the FFC process [37] have attracted the major part of the investment and academic coverage towards developing different routes using the conventional halide precursor or titanium dioxide, respectively, as demonstrated in Table 2.

Even though a large number of new processes have been investigated, there is no process to date that can replace Kroll at a commercial scale. Some concepts have been successful at a pilot plant level and companies such as Metalysis are commercializing their developments [47]. However, no process will be able to compete with the conventional one until the economics of scale are achieved [48]. The lack of commercial success can be partially attributed to industry's immobilism. There is an interest in the industry for more affordable titanium but there is also a need of amortizing the current plants and investment. Allanore [49] argues, "if you don't pay for the environmental costs, and you have a steel plant that needs to be valuable for the next 30 years, there is no way you're going to change your technology". Nevertheless, the current push for sustainability growth and environmental awareness are reasons to be optimistic.

For the foreseeable future, an electrochemical process for the extraction of titanium is the route with the highest potential to displace the Kroll process [50]. The use of electricity eliminates the costly stage of separating the reducing agent from the product. This technology is being improved over decades, but suitable electrolytic cells for the electrowinning of titanium has not been scaled up yet [51]. This work aims to deepen and broaden the initially established scientific knowledge by developing a process for the direct extraction of titanium from a slag by ultra-high-temperature electrolysis.

[1] Titanium sponge is the raw form of titanium metal produced via the Kroll process. The further processing required to create a finished part accounts for approximately half of the overall cost [46,52].

4 Redefining waste in NZ

Conventional steelmaking processing is dominated by the reduction of haematite (Fe_2O_3) in blast furnaces [3]. Nevertheless, titanium-bearing iron ores are an alternative source of iron. China, which holds approximately 50% of the total titanium reserve in the world, has about 98% in the form of vanadium-titanium magnetite ores [44]. New Zealand holds more than 150 million tonnes of ironsand [5]. The slag or undesirable impurities, mainly oxides, resulting from the reduction and separation of iron from those ores, are tapped off periodically [53] and dumped without further mineral extraction. The chemical composition of NZS ironmaking slag was investigated using XRF [22].

Table 3: Chemical composition of NZS's ironmaking slag (wt. %).

TiO_2	Al_2O_3	CaO	SiO_2	MgO	FeO	MnO	V_2O_5
32.5	18.5	16.4	13.8	13.6	4.3	0.9	0.2

Based on the vast quantities of TiO_2 available as part of the slag shown in Table 3 and the current titanium price [4], slag predominately used in road construction [11] should be considered a "waste". Research conducted to improve the utilization of titanomagnetite ores have determined the difficulty of recovering metallic iron and titanium through traditional separation processes [54]. She et al. attributes that to the scattered distribution of titanium components in various mineral phases with complex interfacial combination [55]. X-ray diffraction was used to confirm that complex phase identification [56]. The results in Figure 1 show an array of at least 4 primary mineral phases: perovskite ($CaTiO_3$), armalcolite ($Mg_{0.5}Fe_{0.5})Ti_2O_5$), magnesium iron aluminate ($Mg(Fe_{0.6}Al_{1.4})O_4$) and calcium magnesium silicate ($Ca_{0.8}Mg_{1.2}Si_2O_6$).

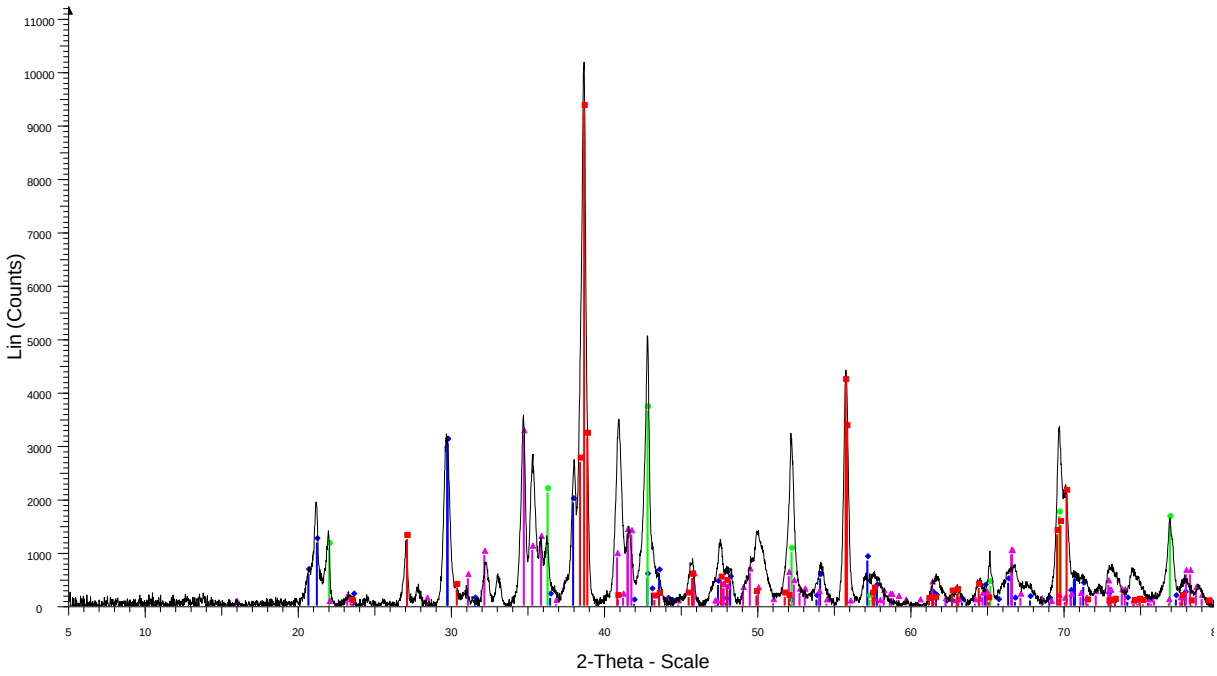

Figure 1: XRD analysis of NZS's ironmaking slag showing perovskite (red), armalcolite (blue), magnesium iron aluminate (green) and calcium magnesium silicate (pink).

Recently, molten oxides have been proven as candidate electrolytes for high-temperature, carbon-free metal electrolytic production [42,57]. This promising route has been demonstrated by recent research conducted by prestigious institutions and published in the highest ranking international journals [37,58]. Thus, this work intends to explore the features and challenges of the direct electrolytic extraction of titanium from NZS ironmaking slag.

The novel approach in this work relies on upgrading waste slag material to high-value, high-purity titanium metal. The disruptive idea of this project is to develop a technology with improved efficiency, sustainability and scalability by using the molten slag directly from the process at approximately 1750 K. Aluminium's change from precious metal to commodity has demonstrated that electrochemical processing can satisfy those criteria [50]. Moreover, electrolysis in the molten state, when electricity comes from a renewable source, shows excellent cost efficiency and a low carbon footprint.

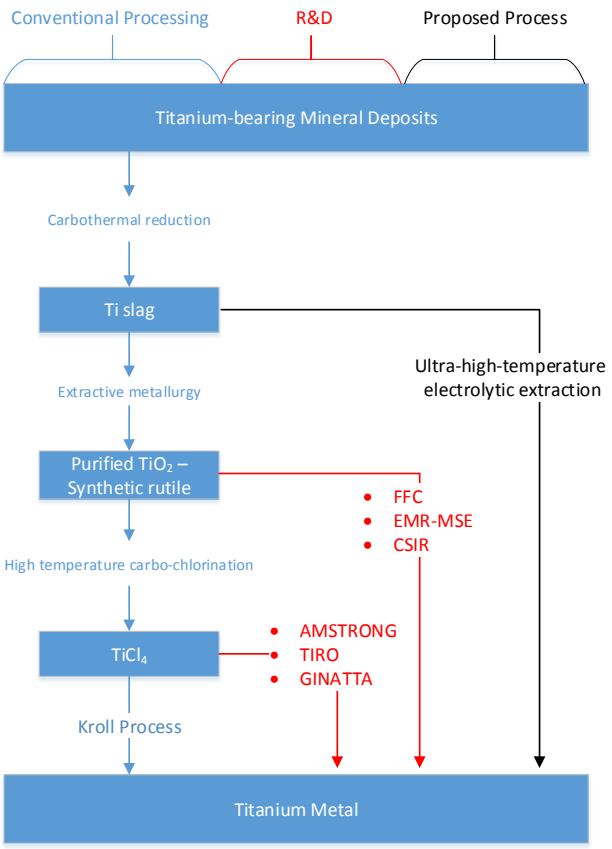

Figure 2: Comparison of processes illustrating the proposed process simplification, modified according to [59].

Electrolytic separation of titanium metal using the waste material directly from NZS's process, in its molten state, is a game changing opportunity. Figure 2 illustrates the potential for reducing the process to a single stage. Additionally, since New Zealand does not currently have the capability to manufacture titanium metal, the development of such a process will provide a secure supply for the growing demand for this resource while it inevitably strengthens the steelmaking industry by extracting greater value from a natural resource.

5 Ultra-high-temperature electrolytic titanium extraction from slag

Electrolysis dates from the beginning of the 19th century after the discovery of a continuous source of electric current by Alessandro Volta [60]. In 1808, the decomposition of molten potash to potassium is credited to be the first demonstration of electricity's ability to isolate metals [61]. Since then, metallurgical electrochemistry has expanded to the point of being the only commercially viable means for the extraction of metals, e.g. aluminium, to compete with thermochemical processes, e.g. magnesium, and even to be considered for the future of extra-terrestrial metal extraction [62]. Today, 33 out of 70 of the most common metallic elements are electrolytically produced [50].

5.1 Features and challenges

The electrolytic manufacturing of titanium is attractive because titanium is the most abundant refractory metal and it has a high near-term market potential [63]. Furthermore, the capital and operating cost of electric power are not new to the conventional titanium extraction processes. Molten salt electrolysis is used in the conventional industrial processes [48]; however, electrochemical processing of titanium has some major differences with some well-established practices such as aluminium processing, which makes it more challenging. The melting point of titanium is 1273 K higher than aluminium. The typical operating temperature of electrolytic cells to electrowin lithium, sodium and magnesium are 723, 853 and 853 K respectively, while for titanium it would have to be above 1933 K to have liquid metal as a product [52]. If the product is solid, there is another obstacle to overcome since solid state deposition tends to result in nucleation and dendrite formation, which facilitates reoxidation [46]. Additionally, aluminium has only one stable valence while titanium has several [64]. The resulting loss of efficiency plus the possibility of titanium being contaminated with carbon calls for more restrictive measures and makes the mechanical design of the electrochemical cell a more demanding and complex task than for the commercially successful Hall-Heroult process [51].

To create an electrolytic process which is the real analogue to aluminium's Hall-Heroult process, first a suitable electrolyte needs to be found [65]. Metal reactivity delimits the choice of electrolyte [66], which is the process enabler [50]. Aqueous electrolytes are used for the more noble metals while molten salts for the more reactive. Zinc, copper and cobalt are examples of metals extracted from aqueous solutions [67]. In this process the cell temperature is relatively low (308 K for zinc and copper, and 323-338 K for cobalt [67]) but the concentrated ore must undergo different stages before electrolysis (e.g. leaching, purification). Electrolysis in aqueous media could never work for titanium since hydrogen is more noble and the electrolysis would result in the liberation of hydrogen and oxygen [46].

The use of molten salts for electrolytic extraction has its hallmark in the Hall-Heroult process for aluminium [50]. Liquid metal is obtained by an electrolytic reduction of alumina in a molten cryolite (81 wt. % Na_3AlF_6, 11 wt. % AlF_3, 5 wt. % CaF_2) bath at 1233 K, where 60% of the electrolytic extraction cost comes from electricity [60]. Electricity's low cost, simple process and continuous mode of operations has allowed it to become the main route to aluminium metal. However, the fact that some electrochemical processing techniques are industrially mature practices does not prevent the presence of unresolved challenges. In aluminium processing, the lack of suitable materials for the construction of the Hall-Heroult cell presents a limitation in the productivity of the process [61]. Furthermore, it is far from being a carbon-free extraction technology. The carbon consumption (0.45 kg C / 1 kg Al) is the main concern, and so the quest for a non-consumable anode has become the ultimate material challenge [68].

Sadoway [65] realized that a change of paradigm was going to be needed to cope with the new constrains. Following a conventional methodology would be an obstacle limiting the development of a technology that is environmentally respectful and produces less expensive titanium. His group at MIT was one of the first to use a molten oxide feedstock as an electrolyte. The so called molten oxide electrolysis enables the production of liquid metal and oxygen resulting in a process simplification and a reduction in energy consumption and CO_2 emission [58]. The direct electrolysis of an oxide ore or a slag to obtain metal and oxygen has attracted organizations like NASA and the U.S. NAVY who, intrigued by the possibilities that a newly developed process could offer, have financed its study [42,62]. Furthermore, big international companies have realized that and have started to patent their developments [41]. Literature motivates experimental exploration to verify the feasibility of using NZS ironmaking slag as an electrolyte.

6 Conclusions and recommendations

In this paper, the extraction of further value from a waste stream has been studied. Emphasis has been placed on understanding the unique features of ironmaking slag obtained from the processing of ironsands. The recycling possibilities have been discussed and the electrolytic extraction of titanium from the slag has proven to be an excellent candidate from the point of view of increasing value while being environmentally responsible. With all this potential, it is reasonable to ask why the use of molten oxides as electrolytes has not gained more relevance as an alternative to traditional processing. The answer may be motivated by the cost, scarce information available and constraints in the choice of materials for construction [57]. Nonetheless, new opportunities are emerging with advances in the field of environmental regulation. Traditional practices are starting to assume the cost associated with the emission of CO_2 to the atmosphere [3]. Advances in material science, tailoring the composition and structure of materials can overcome the electrolytic cell's construction difficulties. The current push for sustainable growth can portend the renaissance of this technology, facilitating clean electrochemical technology to replace the current one, which is incapable of meeting tighter specifications.

Extensive experimental research needs to be conducted to verify the feasibility of the proposed hypothesis. This novel approach will be demonstrated in a purpose-built, lab-scale, ultra-high temperature electrolytic cell. Additionally, future work will address the still insufficient theoretical understanding of titanium electrical behavior in complex oxide systems [69] and develop an understanding of the interactions of the different components in such systems.

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